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(54) Title: DETERGENT COMPOSITIONS COMPRISIN	1G CH	OLESTEROL ESTERASE					
(57) Abstract							
The present invention relates to detergent composit esterase.	ions in	cluding laundry and diswashing compositions co	omprising a cholesterol				
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DETERGENT COMPOSITIONS COMPRISING CHOLESTEROL ESTERASE

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Field of the Invention

The present invention relates to detergent compositions, including laundry and dishwashing compositions, comprising a cholesterol esterase enzyme.

Background of the invention

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The overall performance of a detergent product for use in washing or cleaning method such as laundry or dishwashing, is judged by a number of factors, including the ability to remove greasy / oily soils and the ability to prevent redeposition of the soils or the breakdown products of the soils on the articles in the wash.

The complex nature of everyday "body" soils typically found on pillow cases, T-shirts, collars and socks, provides a thorough cleaning challenge for detergents. These soils are difficult to remove completely and often residues build up on fabric leading to dinginess and yellowing.

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Greasy / oily soils and stains represent also a well-known cleaning challenge often met by the inclusion of lipolytic enzymes in detergent compositions. Lipolytic enzymes for enhanced removal of triglycerides containing soils and stains from fabrics are indeed well-known in the art. Examples are US Patent 4,769,173; US Patent 5,069,809; WO 94/03578; WO 96/12004; WO 96/16153, .

It is therefore an object of the present invention to provide detergent compositions, including laundry and dishwashing compositions which provide cleaning performance on body soils and/or oily / greasy soils and stains.

The above objective has been met by formulating detergent compositions, including laundry and dishwashing compositions comprising a cholesterol esterase at a level of from 0.0001% to 5%, preferably 0.001% to 2% pure enzyme by weight of total composition.

It is a further object of the invention to provide detergent compositions, including laundry and dishwashing compositions comprising a cholesterol esterase for improved cleaning performance on body soils and/or oily / greasy soils and stains.

The above objective has been met by formulating detergent compositions, including laundry and dishwashing compositions further comprising a surfactant selected from nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants and/or mixtures thereof, a lipolytic and/or proteolytic enzyme, a hydrophobic bleach activator, a soil release polymer and/or a dispersant.

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It has been indeed surprisingly found that cholesterol esterase is an enzyme which boosts cleaning performance by hydrolysing the cholesterol esters present in body soils and/or greasy / oily soils and stains. It is believed that said enzymatic hydrolysis products are rendered more soluble and their removal by the detergent actives is thereby facilitated.

Cholesterol esterase is commonly used in the medical context of cholesterol diagnostic and treatment such as described in J08116996, AU 9 534 240, EP 709 456, US 5 484 777, US 5 474 993, J07222586, J07070102, J07069885 and AU 9 466 101.

WO 94/23052 describes a method of hydrolysing cholesterol esters by treating the cholesterol esters with a cholesterol esterase enzyme obtained from a strain of Pseudomonas fragi. Said method is useful for the treatment of eggs, papermaking pulp, sterols, lanolin and for cleaning purposes, especially gel cleaning agents for industrial hard surface cleaning. However, the detergent compositions of the present invention have not been exemplified and the cleaning performance on body soils and/or oily / greasy soils and stains of laundry and dishwashing compositions has not been therein recognised.

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Summary of the invention

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The present invention relates to detergent compositions, including laundry and dishwashing compositions, comprising a cholesterol esterase enzyme at a level of from 0.0001% to 5%, preferably 0.001% to 2% pure enzyme by weight of total composition for improved cleaning performance on body soils and/or oily / greasy soils and stains.

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The present invention also relates to detergent compositions, including laundry and dishwashing compositions comprising a cholesterol esterase in combination with a surfactant selected from nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants and/or mixtures thereof, a lipolytic and/or proteolytic

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enzyme, a hydrophobic bleach activator, a soil release polymer and/or a dispersant.

Detailed description of the invention

The cholesterol esterase enzyme

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An essential component of the detergent compositions of the invention is a cholesterol esterase falling under the EC classification EC 3.1.1.13.

This cholesterol esterase is incorporated into the detergent compositions in accordance with the invention at a level of from 0.0001 % to 5%, preferably from 0.001% to 2% pure enzyme by weight of the composition.

Suitable cholesterol esterases for use in the present invention are described in WO 93/10224 and in WO 94/23052 by Novo Nordisk A/S wherein a cholesterol esterase acting lipase from respectively Pseudomonas cepacia or fragi are disclosed and in J07203959 disclosing a DNA encoding a stable cholesterol esterase, related vectors and transformed microbes, for the large scale production of the enzyme.

Commercially available cholesterol esterases are Sigma bovine pancrease Cholesterol esterase (Sigma 3766) or Bohringar Mannheim Pseudomonas fluorescens cholesterol esterase.

Preferred cholesterol esterases are alkaline cholesterol esterases, ie enzymes having an enzymatic activity of at least 10%, preferably 25%, more preferably 40% of its maximum activity at a pH ranging from 7 to 11. More preferred cholesterol esterases are enzymes having their maximum activity at a pH ranging from 7 to 11.

The cholesterol esterase can be produced by the so called wild-type organism or by any host organism in which the gene responsible for the production of the cholesterol esterase, has been cloned and expressed.

Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimise their performance efficiency in the detergent compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

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In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability.

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The surfactant system

The detergent compositions according to the present invention can comprise a surfactant system wherein the surfactant can be selected from nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants.

Indeed, it has been surprisingly found that the combination of cholesterol esterase with a surfactant provides enhanced cleaning performance on body soils and/or oily / greasy soils and stains.

The surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation are 1% to 35% by weight, most preferably from 1% to 30% by weight of detergent compositions in accord with the invention.

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The surfactant is preferably formulated to be compatible with enzyme components present in the composition. In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of any enzyme in these compositions.

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Preferred surfactant systems to be used according to the present invention comprise as a surfactant one or more of the nonionic and/or anionic surfactants described herein.

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include IgepalTM CO-630, marketed by the GAF Corporation; and TritonTM X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type include TergitolTM 15-S-9 (the condensation product of C₁₁-C₁₅

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linear alcohol with 9 moles ethylene oxide), TergitolTM 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; NeodolTM 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), NeodolTM 23-3 (the condensation product of C₁₂-C₁₃ linear alcohol with 3.0 moles of ethylene oxide), NeodolTM 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), NeodolTM 45-5 (the condensation product of C₁₄-C₁₅ linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, KyroTM EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O3O or O5O (the condensation product of C₁₂-C₁₄ alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

The preferred alkylpolyglycosides have the formula

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wherein ${\sf R}^2$ is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl

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groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

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The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available PlurafacTM LF404 and PluronicTM surfactants, marketed by BASF.

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Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic TM compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C₈-C₁₄ alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C₈-C₁₈ alcohol ethoxylates (preferably C₁₀ avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula.

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wherein R^1 is H, or R^1 is C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R^1 is methyl, R^2 is a straight C_{11-15} alkyl or C_{16-18} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

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Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C₈-C₂₀ carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO₃ according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula:

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wherein R^3 is a C_8 - C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a C_1 - C_6 hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R^3 is C_{10} - C_{16} alkyl, and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R^3 is C_{10} - C_{16} alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula ROSO₃M wherein R preferably is a C₁₀-C₂₄ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C₁₀-C₂₀ alkyl component, more preferably a C₁₂-C₁₈ alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C₁₂-C₁₆ are preferred for lower wash temperatures (e.g. below about 50°C) and C₁₆₋₁₈ alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for detersive purposes can also be included in the detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of C8-C22 primary of secondary soap, alkanesulfonates, olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British specification No. patent 1,082,179, C8-C24 alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol

sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C₁₂-C₁₈ monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C₆-C₁₂ diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula RO(CH₂CH₂O)_k-CH₂COO-M+ wherein R is a C₈-C₂₂ alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

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When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.

Highly preferred anionic surfactants include alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula RO(A)_mSO3M wherein R is an unsubstituted C₁₀-C₂₄ alkyl or hydroxyalkyl group having a C10-C24 alkyl component, preferably a C12-C20 alkyl or hydroxyalkyl, more preferably C12-C18 alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl

piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12} - C_{18} alkyl polyethoxylate (1.0) sulfate (C_{12} - C_{18} E(1.0)M), C_{12} - C_{18} alkyl polyethoxylate (2.25) sulfate (C_{12} - C_{18} E(2.25)M), C_{12} - C_{18} alkyl polyethoxylate (3.0) sulfate (C_{12} - C_{18} E(3.0)M), and C_{12} - C_{18} alkyl polyethoxylate (4.0) sulfate (C_{12} - C_{18} E(4.0)M), wherein M is conveniently selected from sodium and potassium.

The detergent compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

15 Cationic detersive surfactants suitable for use in the detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula:

$$[R^{2}(OR^{3})_{V}][R^{4}(OR^{3})_{V}]_{2}R^{5}N + X_{-}$$

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wherein R^2 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; each R^4 is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups, -CH₂CHOH-CHOHCOR⁶CHOHCH₂OH wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Quaternary ammonium surfactant suitable for the present invention has the formula (I):

$$R_1$$
 Q
 R_2
 R_3
 R_4
 R_5
 R_5
 R_5

Formula I

whereby R1 is a short chainlength alkyl (C6-C10) or alkylamidoalkyl of the formula (II) :

$$C_6 \cdot C_0$$
 $C_1 \cdot C_2 \cdot C_2 \cdot C_2 \cdot C_1 \cdot C_2 \cdot C_1 \cdot C_1 \cdot C_2 \cdot C_1 \cdot C_1$

Formula II

y is 2-4, preferably 3.

whereby R2 is H or a C1-C3 alkyl,

whereby x is 0-4, preferably 0-2, most preferably 0, whereby R3, R4 and R5 are either the same or different and can be either a short chain alkyl (C1-C3) or alkoxylated alkyl of the formula III,

whereby X^- is a counterion, preferably a halide, e.g. chloride or methylsulfate.

$$($$
 O $)_{z}^{H}$

Formula III

R6 is C₁-C₄ and z is 1 or 2.

Preferred quat ammonium surfactants are those as defined in formula I whereby

 R_1 is C_8 , C_{10} or mixtures thereof, x = 0, R_3 , $R_4 = CH_3$ and $R_5 = CH_2CH_2OH$.

Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula:

$$R_1R_2R_3R_4N + X^-$$
 (i)

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wherein R₁ is C₈-C₁₆ alkyl, each of R₂, R₃ and R₄ is independently C₁-C₄ alkyl, C₁-C₄ hydroxy alkyl, benzyl, and - $(C_2H_{40})_XH$ where x has a value from 2 to 5, and X is an anion. Not more than one of R₂, R₃ or R₄ should be benzyl.

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The preferred alkyl chain length for R_1 is C_{12} - C_{15} particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R_2R_3 and R_4 are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are:

coconut trimethyl ammonium chloride or bromide;
coconut methyl dihydroxyethyl ammonium chloride or bromide;
decyl triethyl ammonium chloride;
decyl dimethyl hydroxyethyl ammonium chloride or bromide;
C12-15 dimethyl hydroxyethyl ammonium chloride or bromide;
coconut dimethyl hydroxyethyl ammonium chloride or bromide;
myristyl trimethyl ammonium methyl sulphate;
lauryl dimethyl benzyl ammonium chloride or bromide;
lauryl dimethyl (ethenoxy)4 ammonium chloride or bromide;
choline esters (compounds of formula (i) wherein R1 is
CH2-CH2-O-C-C12-14 alkyl and R2R3R4 are methyl).

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di-alkyl imidazolines [compounds of formula (i)].

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

Typical cationic fabric softening components include the waterinsoluble quaternary-ammonium fabric softening actives, the most commonly used having been di-long alkyl chain ammonium chloride or methyl sulfate.

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Preferred cationic softeners among these include the following:

1) ditallow dimethylammonium chloride (DTDMAC);

- 2) dihydrogenated tallow dimethylammonium chloride;
- 3) dihydrogenated tallow dimethylammonium methylsulfate;
- 4) distearyl dimethylammonium chloride;
- 5) dioleyl dimethylammonium chloride;
- 6) dipalmityl hydroxyethyl methylammonium chloride;
- 7) stearyl benzyl dimethylammonium chloride;
- 10 8) tallow trimethylammonium chloride;
 - 9) hydrogenated tallow trimethylammonium chloride;
 - 10) C₁₂₋₁₄ alkyl hydroxyethyl dimethylammonium chloride;
 - 11) C₁₂₋₁₈ alkyl dihydroxyethyl methylammonium chloride;
 - 12) di(stearoyloxyethyl) dimethylammonium chloride (DSOEDMAC);
 - 13) di(tallowoyloxyethyl) dimethylammonium chloride;
 - 14) ditallow imidazolinium methylsulfate;
 - 15) 1-(2-tallowylamidoethyl)-2-tallowyl imidazolinium methylsulfate.

Biodegradable quaternary ammonium compounds have been presented as alternatives to the traditionally used di-long alkyl chain ammonium chlorides and methyl sulfates. Such quaternary ammonium compounds contain long chain alk(en)yl groups interrupted by functional groups such as carboxy groups. Said materials and fabric softening compositions containing them are disclosed in numerous publications such as EP-A-0,040,562, and EP-A-0,239,910.

The quaternary ammonium compounds and amine precursors herein have the formula (I) or (II), below:

(1)

wherein Q is selected from -O-C(O)-, -C(O)-O-, -O-C(O)-O-, -NR 4 -C(O)-, -C(O)-NR 4 -;

 R^1 is $(CH_2)_{n}$ -Q- T^2 or T^3 ;

 R^2 is $(CH_2)_{m}$ -Q- T^4 or T^5 or R^3 ;

R3 is C1-C4 alkyl or C1-C4 hydroxyalkyl or H;

R4 is H or C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl;

T1, T2, T3, T4, T5 are independently C11-C22 alkyl or alkenyl;

n and m are integers from 1 to 4; and

10 X⁻ is a softener-compatible anion.

Non-limiting examples of softener-compatible anions include chloride or methyl sulfate.

The alkyl, or alkenyl, chain T¹, T², T³, T⁴, T⁵ must contain at least 11 carbon atoms, preferably at least 16 carbon atoms. The chain may be straight or branched.

Tallow is a convenient and inexpensive source of long chain alkyl and alkenyl material. The compounds wherein T¹, T², T³, T⁴, T⁵ represents the mixture of long chain materials typical for tallow are particularly preferred.

Specific examples of quaternary ammonium compounds suitable for use in the aqueous fabric softening compositions herein include:

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- 1) N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
- N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;
- 3) N,N-di(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 30 4) N,N-di(2-tallowyl-oxy-ethylcarbonyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
 - 5) N-(2-tallowyl-oxy-2-ethyl)-N-(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 35 6) N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
 - 7) N-(2-tallowyl-oxy-2-oxo-ethyl)-N-(tallowyl-N,N-dimethyl-ammonium chloride; and

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8) 1,2-ditallowyl-oxy-3-trimethylammoniopropane chloride; and mixtures of any of the above materials.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

Zwitterionic surfactants are also suitable for use in detergent compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

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When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected

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from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms. Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula

0 \uparrow $R^3 (OR^4) \times N (R^5) 2$

wherein R³ is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R⁴ is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R⁵ is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R⁵ groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C₁₀-C₁₈ alkyl dimethyl amine oxides and C₈-C₁₂ alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

The detergent composition of the present invention may further comprise a cosurfactant selected from the group of primary or tertiary amines.

Suitable primary amines for use herein include amines according to the formula R₁NH₂ wherein R₁ is a C₆-C₁₂, preferably C₆-C₁₀ alkyl chain or

 $R_4X(CH_2)_n$, X is -0-,-C(0)NH- or -NH-, R_4 is a C_6 - C_{12} alkyl chain n is between 1 to 5, preferably 3. R_1 alkyl chains may be straight or branched and may be interrupted with up to 12, preferably less than 5 ethylene oxide moieties.

Preferred amines according to the formula herein above are n-alkyl amines. Suitable amines for use herein may be selected from 1-hexylamine, 1-octylamine, 1-decylamine and laurylamine. Other preferred primary amines include C8-C10 oxypropylamine, octyloxypropylamine, 2-ethylhexyloxypropylamine, lauryl amido propylamine and amido propylamine.

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Suitable tertiary amines for use herein include tertiary amines having the formula R₁R₂R₃N wherein R1 and R2 are C₁-C₈ alkylchains or

$$-(CH_2-CH-O)_{xH}$$

R3 is either a C6-C12, preferably C6-C10 alkyl chain, or R3 is R4X(CH2)n, whereby X is -O-, -C(0)NH- or -NH-,R4 is a C4-C12, n is between 1 to 5, preferably 2-3. R5 is H or C1-C2 alkyl and x is between 1 to 6. R3 and R4 may be linear or branched; R3 alkyl chains may be interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

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Preferred tertiary amines are R₁R₂R₃N where R1 is a C6-C12 alkyl chain, R2 and R3 are C1-C3 alkyl or

$$-(CH_2-CH-C)_{xH}$$

where R5 is H or CH3 and x = 1-2.

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Also preferred are the amidoamines of the formula:

$$R_1 - C - NH - (CH_2) - N - (R_2)_2$$

wherein R_1 is C_6 - C_{12} alkyl; n is 2-4, preferably n is 3; R_2 and R_3 is C_1 - C_4

Most preferred amines of the present invention include 1-octylamine, 1-hexylamine, 1-decylamine, 1-dodecylamine, C8-10oxypropylamine, N coco

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1-3diaminopropane, coconutalkyldimethylamine, lauryldimethylamine, lauryl bis(hydroxyethyl)amine, coco bis(hydroxyehtyl)amine, lauryl amine 2 moles propoxylated, octyl amine 2 moles propoxylated, lauryl amidopropyldimethylamine, C8-10 amidopropyldimethylamine and C10 amidopropyldimethylamine.

The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecyldimethylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

The lipolytic enzyme

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It has also been surprisingly found that the combination of cholesterol esterase with a lipolytic enzyme provides enhanced cleaning performance on body soils and/or oily / greasy soils and stains.

In the present context, the term "lipolytic enzyme" is intended to indicate an enzyme exhibiting a lipid degrading capability, such as a capability of degrading a triglyceride, a phospholipid, a wax-ester or cutin. The lipolytic enzyme may, e.g., be a lipase, a phospholipase, an esterase or a cutinase.

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Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism Pseudomonas fluorescent IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex Chromobacter viscosum, e.g. Chromobacter viscosum var. lipolyticum NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; Chromobacter viscosum lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex

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Pseudomonas gladioli. Especially suitable lipases are lipases such as M1 Lipase R and Lipomax R (Gist-Brocades) and Lipolase R and Lipolase Ultra R (Novo) which have found to be very effective when used in combination with the compositions of the present invention.

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Preferred lipolytic enzymes include variants of lipolytic enzymes producible by Humicola lanuginosa and Thermomyces lanuginosus, or by cloning and expressing the gene responsible for producing said variants into a host organism, e.g. Aspergillus oryzae as described in European Patent Application 0 258 068, incorporated herein by reference.

Other preferred lipolytic enzymes are variants of the native lipase derived from Humicola lanuginosa as described in US Serial No. 08/341,826. Preferably the Humicola lanuginosa strain DSM 4106 is used. An example of said variants is D96L lipolytic enzyme as described in patent application WO 92/05249.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Suitable cutinases are described in WO 94/14963 and WO 94/14964. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor).

Other suitable second lipolytic enzymes are phospholipases and esterases.

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The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

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The proteolytic enzyme

It has also been surprisingly found that the combination of cholesterol esterase with a proteolytic enzyme provides enhanced cleaning performance on body soils and/or oily / greasy soils and stains.

Suitable proteases are the subtilisins which are obtained from particular strains of B. subtilis and B. licheniformis (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of Bacillus, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB Other suitable proteases include ALCALASE®, 1,243,784 to Novo. DURAZYM® and SAVINASE® from Novo and MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine protealytic enzyme which is called "Protease A" herein. More preferred is what is called herein "Protease C", which is a variant of an alkaline serine protease from Bacillus in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein. See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 93/18140 A to Enzymatic detergents comprising protease, one or more other Novo. enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo.

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In more detail, protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104,

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+107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of Bacillus amyloliquefaciens subtilisin, as described in WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994. Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO91/06637 and protease BLAP® described in WO91/02792.

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The proteolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

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The Hydrophobic bleach activator

It has also been surprisingly found that the combination of cholesterol esterase with a hydrophobic bleach activator provides enhanced cleaning performance on body soils and/or oily / greasy soils and stains.

An essential element of the present invention is a hydrophobic bleach activator within a bleaching system. The bleaching system wherein a bleach activator is used, also comprises as an essential component a peroxygen bleach capable of releasing hydrogen peroxide in aqueous solution.

It is generally believed that the bleach activator indergoes nucleophilic attack by a perhydroxide anion, which is generated from the hydrogen peroxide evolved by the peroxygen bleach, to form a peroxycarboxylic acid. This reaction is commonly referred to as perhydrolysis.

The detergent compositions of the present invention include bleaching agents such as hydrogen peroxide, PB1, PB4 and percarbonate with a particle size of 400-800 microns. These bleaching agent components can include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators.

When present oxygen bleaching compounds will typically be present at levels of from about 1% to about 25%.

The hydrogen peroxide releasing agents are used in combination with bleach activators such as nonanoyloxybenzene-sulfonate (NOBS, described in US 4,412,934), 3,5,-trimethylhexanoloxybenzenesulfonate (ISONOBS, described in EP 120,591)or Phenolsulfonate ester of N-nonanoyl-6-aminocaproic acid (NACA-OBS, described in WO94/28106), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect. Their acid form can also be used such as the nonyl amide of peroxy succinic acid, nonylamide of peroxy adipic acid or nonanoyl oxybenzene peroxy acid as described in our co-pending application USSN 08/136,626.

Useful bleaching agents, including peroxyacids and bleaching systems comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention as the N-acyl lactam bleach described in WO95/27773 and some bleach activators disclosed in our co-pending application PCT/US95/07823 USSN.

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The dispersant

It has also been surprisingly found that the combination of cholesterol esterase with a dispersant provides enhanced cleaning performance on body soils and/or oily / greasy soils and stains.

Suitable dispersant for the detergent composition of the present invention: Suitable water-soluble organic salts are the homo- or copolymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 1,000 to 100,000.

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Especially, copolymer of acrylate and methylacrylate such as the 480N having a molecular weight of 4000, at a level from 0.5-20% by weight of composition can be added in the detergent compositions of the present invention.

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Other suitable dispersant for the detergent compositions of the invention is a lime soap dispersant compound, which has a lime soap dispersing power (LSDP), as defined hereinafter of no more than 8, preferably no more than 7, most preferably no more than 6. The lime soap dispersant compound is present at a level of from 0.1% to 40% by weight, more preferably 1% to 20% by weight, most preferably from 2% to 10% by weight of the compositions.

A lime soap dispersant is a material that prevents the precipitation of alkali metal, ammonium or amine salts of fatty acids by calcium or magnesium ions. A numerical measure of the effectiveness of a lime soap dispersant is given by the lime soap dispersing power (LSDP) which is determined using the lime soap dispersion test as described in an article by H.C. Borghetty and C.A. Bergman, J. Am. Oil. Chem. Soc., volume 27, pages 88-90, (1950). This lime soap dispersion test method is widely used by practitioners in this art field being referred to , for example, in the following review articles; W.N. Linfield, Surfactant Science Series, Volume 7, p3; W.N. Linfield, Tenside Surf. Det., Volume 27, pages 159-161, (1990); and M.K. Nagarajan, W.F. Masler, Cosmetics and Toiletries, Volume 104, pages 71-73, (1989). The LSDP is the % weight ratio of dispersing agent to sodium oleate required to disperse the lime soap deposits formed by 0.025g of sodium oleate in 30ml of water of 333ppm CaCO₃ (Ca:Mg = 3:2) equivalent hardness.

In the Borghetty/Bergman lime soap dispersion test 5ml of a 0.5% by weight solution of sodium oleate is added to a test tube, followed by 10ml of a hard water solution containing 600ppm Ca²⁺ and 400ppm Mg²⁺ (1000ppm as CaCO₃ equivalent, 70° Clark Hardness) which will cause formation of a lime soap deposit (or curd). An arbitrary amount (less than 15ml) of dispersing agent as a 0.25% by weight solution is then added to the test tube. The total volume of solution in the test tube is then made up to 30ml and the test tube is stoppered, inverted 20 times and then allowed

to stand for 30 seconds. The contents of the test tube are then visually inspected to check if the lime soap deposits are still intact or whether they have been dispersed into the solution. The test procedure is repeated using different amounts of dispersing agent solution until the minimum amount of dispersing agent solution which will cause dispersion of the lime soap deposits is obtained.

The lime soap dispersing power is then obtained as:

10 LSDP = (weight of lime soap dispersing agent) x 100 (weight of sodium oleate)

Thus in accord with the test method described above a material with a lower LSDP is a more effective lime soap dispersant than one with a higher LSDP.

A listing of suitable lime soap dispersants for use in accord with the invention is given in the above mentioned review by M. Linfield to be found in Tenside. Sust. Det., Volume 27, pages 159-161 (1990).

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Polymeric lime soap dispersants suitable for use herein are described in the above mentioned article by M.K. Nagarajan and W.F. Masler, to be found in Cosmetics and Toiletries, Volume 104, pages 71-73, (1989). Examples of such polymeric lime soap dispersants include certain water-soluble salts of copolymers of acrylic acid, methacrylic acid or mixtures thereof, and an acrylamide or substituted acrylamide, where such polymers typically have a molecular weight of from 5,000 to 20,000.

Surfactants having good lime soap dispersant capability will include certain amine oxides, betaines, sulfobetaines, alkyl ethoxysulfates and ethoxylated alcohols.

Exemplary surfactants having a LSDP of no more than 8 for use in accord with the invention include C_{16} - C_{18} dimethyl amine oxide, C_{12} - C_{18} alkyl ethoxysulfates with an average degree of ethoxylation of from 1-5, particularly C_{12} - C_{15} alkyl ethoxysulfate surfactant with a degree of ethoxylation of about 3 (LSDP=4), and the C_{13} - C_{15} ethoxylated alcohols

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with an average degree of ethoxylation of either 12 (LSDP = 6) or 30, sold under the trade names Lutensol A012 and Lutensol A030 respectively, by BASF GmbH.

Polymeric lime soap peptisers suitable for use herein are described in the article by M.K. Nagarajan, W.F. Masler, to be found in Cosmetics and Toiletries, volume 104, pages 71-73, (1989).

Hydrophobic bleaches such as 4-[N-octanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-nonanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-decanoyl-6-aminohexanoyl]benzene sulfonate and mixtures thereof; and nonanoyloxy benzene sulfonate together with hydrophilic / hydrophobic bleach formulations can also be used as lime soap peptisers compounds.

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The soil release polymer

It has also been surprisingly found that the combination of cholesterol esterase with a soil release polymer hereinafter "SRP", provides enhanced cleaning performance on body soils and/or oily / greasy soils and stains.

SRP's will generally be comprised from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the compositions.

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Preferred SRP's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles, thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the SRP to be more easily cleaned in later washing procedures.

SRP's can include a variety of charged, e.g., anionic or even cationic species, see U.S. 4,956,447, issued September 11, 1990 to Gosselink, et al., as well as noncharged monomer units, and their structures may be linear, branched or even star-shaped. They may include capping moieties

which are especially effective in controlling molecular weight or altering the physical or surface-active properties. Structures and charge distributions may be tailored for application to different fiber or textile types and for varied detergent or detergent additive products.

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Preferred SRP's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without, of course, forming a densely crosslinked overall structure.

Suitable SRP's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and allyl-derived sulfonated terminal moieties covalently attached to the backbone, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Such ester oligomers can be prepared by: (a) ethoxylating allyl alcohol; (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2propylene glycol ("PG") in a two-stage transesterification/oligomerization procedure; and (c) reacting the product of (b) with sodium metabisulfite in SRP's water. Other include the nonionic end-capped propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al., for example those produced by transesterification / oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Other examples of SRP's include: the partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, methyl (Me)-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al., the latter being typical of SRP's useful in both laundry and

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fabric conditioning products, an example being an ester composition made from m-sulfobenzoic acid monosodium salt, PG and DMT, optionally but preferably further comprising added PEG, e.g., PEG 3400.

SRP's also include: simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; the C₁-C₄ alkyl celluloses and C₄ hydroxyalkyl celluloses, see U.S. 4,000,093, December 28, 1976 to Nicol, et al.; and the methyl cellulose ethers having an average degree of substitution (methyl) per anhydroglucose unit from about 1.6 to about 2.3 and a solution viscosity of from about 80 to about 120 centipoise measured at 20°C as a 2% aqueous solution. Such materials are available as METOLOSE SM100 and METOLOSE SM200, which are the trade names of methyl cellulose ethers manufactured by Shinetsu Kagaku Kogyo KK.

Suitable SRP's characterised by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ vinyl esters, preferably poly(vinyl acetate), grafted onto polyalkylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available examples include SOKALAN SRP's such as SOKALAN HP-22, available from BASF, Germany. Other SRP's are polyesters with repeat units containing 10-15% by weight of ethylene terephthalate together with 80-90% by weight of polyoxyethylene terephthalate derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Commercial examples include ZELCON 5126 from Dupont and MILEASE T from ICI.

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Another preferred SRP is an oligomer having empirical formula (CAP)₂(EG/PG)₅(T)₅(SIP)₁ which comprises terephthaloyl (T), sulfoisophthaloyl (SIP), oxyethyleneoxy and oxy-1,2-propylene (EG/PG) units and which is preferably terminated with end-caps (CAP), preferably modified isethionates, as in an oligomer comprising one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a defined ratio, preferably about 0.5:1 to about 10:1, and two end-cap units

derived from sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said SRP preferably further comprises from 0.5% to 20%, by weight of the oligomer, of a crystallinity-reducing stabiliser, for example an anionic surfactant such as linear sodium dodecylbenzenesulfonate or a member selected from xylene-, cumene-, and toluene- sulfonates or mixtures thereof, these stabilizers or modifiers being introduced into the synthesis vessel, all as taught in U.S. 5,415,807, Gosselink, Pan, Kellett and Hall, issued May 16, 1995. Suitable monomers for the above SRP include Na-2-(2-hydroxyethoxy)-ethanesulfonate, DMT, Na-dimethyl-5-sulfoisophthalate, EG and PG.

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Yet another group of preferred SRP's are oligomeric esters comprising: (1) a backbone comprising (a) at least one unit selected from the group consisting of dihydroxysulfonates, polyhydroxy sulfonates, a unit which is at least trifunctional whereby ester linkages are formed resulting in a branched oligomer backbone, and combinations thereof; (b) at least one unit which is a terephthaloyl moiety; and (c) at least one unsulfonated unit which is a 1,2-oxyalkyleneoxy moiety; and (2) one or more capping units selected from nonionic capping units, anionic capping units such as alkoxylated, preferably ethoxylated, isethionates, alkoxylated propanesulfonates, alkoxylated propanedisulfonates, alkoxylated phenolsulfonates, sulfoaroyl derivatives and mixtures thereof. Preferred are esters of the empirical formula:

{(CAP)x(EG/PG)y'(DEG)y"(PEG)y"'(T)z(SIP)z'(SEG)q(B)m}

wherein CAP, EG/PG, PEG, T and SIP are as defined hereinabove, (DEG) represents di(oxyethylene)oxy units, (SEG) represents units derived from the sulfoethyl ether of glycerin and related moiety units, (B) represents branching units which are at least trifunctional whereby ester linkages are formed resulting in a branched oligomer backbone, x is from about 1 to about 12, y' is from about 0.5 to about 25, y'' is from 0 to about 12, y''' is from 0 to about 10, y' + y'' + y''' totals from about 0.5 to about 25, z is from about 1.5 to about 25, z' is from 0 to about 12; z + z' totals from about 1.5 to about 25, q is from about 0.05 to about 12; m is from about 0.01 to about 10, and x, y', y'', y''', z, z', q and m represent the average

number of moles of the corresponding units per mole of said ester and said ester has a molecular weight ranging from about 500 to about 5,000.

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Preferred SEG and CAP monomers for the above esters include Na-2-(2-,3-dihydroxypropoxy)ethanesulfonate ("SEG"), Na-2-{2-(2hydroxyethoxy) ethoxy} ethanesulfonate ("SE3") and its homologs and mixtures thereof and the products of ethoxylating and sulfonating allyl Preferred SRP esters in this class include alcohol. the product of transesterifying oligomerizing and sodium 2-{2-(2-hydroxyethoxy)ethoxy}ethanesulfonate and/or sodium 2-[2-{2-(2-hydroxyethoxy)ethoxy}ethoxy]ethanesulfonate, DMT, sodium 2-(2,3dihydroxypropoxy) ethane sulfonate, EG, and PG using an appropriate Ti(IV) catalyst and can be designated as (CAP)2(T)5(EG/PG)1.4(SEG)2.5(B)0.13 wherein CAP is (Na+-O3S[CH2CH2O]3.5)- and B is a unit from glycerin and the mole ratio EG/PG is about 1.7:1 as measured by conventional gas chromatography after complete hydrolysis.

Additional classes of SRP's include: (I) nonionic terephthalates using diisocyanate coupling agents to link polymeric ester structures, see U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al.; and (II) SRP's with carboxylate terminal groups made by adding trimellitic anhydride to known SRP's to convert terminal hydroxyl groups to trimellitate esters. With the proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRP's may be used as starting materials as long as they have hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.. Other classes include: (III) anionic terephthalatebased SRP's of the urethane-linked variety, see U.S. 4,201,824, Violland et al.; (IV) poly(vinyl caprolactam) and related co-polymers with monomers such as vinyl pyrrolidone and/or dimethylaminoethyl methacrylate, including both nonionic and cationic polymers, see U.S. 4,579,681, Ruppert et al.; (V) graft copolymers, in addition to the SOKALAN types from BASF, made by grafting acrylic monomers onto sulfonated polyesters. assertedly have soil release and anti-redeposition activity similar to known cellulose ethers: see EP 279,134 A, 1988, to Rhone-Poulenc Chemie. Still other classes include: (VI) grafts of vinyl monomers such as acrylic acid and

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vinyl acetate onto proteins such as caseins, see EP 457,205 A to BASF (1991); and (VII) polyester-polyamide SRP's prepared by condensing adipic acid, caprolactam, and polyethylene glycol, especially for treating polyamide fabrics, see Bevan et al., DE 2,335,044 to Unilever N. V., 1974. Other useful SRP's are described in U.S. Patents 4,240,918, 4,787,989 and 4,525,524.

Other suitables SRP for the purpose of present invention are described in US Patent Nos. US5,541,341; US4,715,990; US5,496,490 and in WO95/32997.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula

(CH₃(PEG)₄₃)_{0.75}(POH)_{0.25}[T-PO)_{2.8}(T-PEG)_{0.4}]T(PO-H)_{0.25}((PEG)₄₃CH₃)_{0.75}

where PEG is -(OC₂H₄)O-,PO is (OC₃H₆O) and T is (pcOC₆H₄CO).

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1.2 diol, about

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10% by weight ethylene glycol about 13% by weight of dimethyl sulfobenzoic acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

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Detergent components

The detergent compositions of the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of

the composition, and the nature of the cleaning operation for which it is to be used.

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The detergent compositions according to the invention can be liquid, paste, gels, bars, tablets, powder or granular forms. Granular compositions can also be in "compact" form, the liquid compositions can also be in a "concentrated" form.

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The compositions of the invention may for example, be formulated as hand and machine dishwashing compositions, hand and machine laundry detergent compositions including laundry additive compositions and compositions suitable for use in the soaking and/or pretreatment of stained fabrics, rinse added fabric softener compositions. Compositions containing such cholesterol esterase can also be formulated as softening compositions.

Such compositions containing cholesterol esterase can provide fabric cleaning, stain removal, whiteness maintenance, softening, color appearance and dye transfer inhibition when formulated as laundry detergent compositions.

When formulated as compositions for use in manual dishwashing methods the compositions of the invention preferably contain a surfactant and preferably other detergent compounds selected from organic polymeric compounds, suds enhancing agents, group II metal ions, solvents, hydrotropes and additional enzymes.

PCT/US96/20876

When formulated as compositions suitable for use in a laundry machine washing method, the compositions of the invention preferably contain both a surfactant and a builder compound and additionally one or more detergent components preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors. Laundry compositions can also contain softening agents, as additional detergent components.

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The compositions of the invention can also be used as detergent additive products. Such additive products are intended to supplement or boost the performance of conventional detergent compositions.

If needed the density of the laundry detergent compositions herein ranges from 400 to 1200 g/litre, preferably 600 to 950 g/litre of composition measured at 20°C.

The "compact" form of the compositions herein is best reflected by density and, in terms of composition, by the amount of inorganic filler salt; inorganic filler salts are conventional ingredients of detergent compositions in powder form; in conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% by weight of the total composition.

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In the compact compositions, the filler salt is present in amounts not exceeding 15% of the total composition, preferably not exceeding 10%, most preferably not exceeding 5% by weight of the composition.

The inorganic filler salts, such as meant in the present compositions are selected from the alkali and alkaline-earth-metal salts of sulphates and chlorides.

A preferred filler salt is sodium sulphate.

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Liquid detergent compositions according to the present invention can also be in a "concentrated form", in such case, the liquid detergent

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compositions according the present invention will contain a lower amount of water, compared to conventional liquid detergents.

Typically the water content of the concentrated liquid detergent is preferably less than 40%, more preferably less than 30%, most preferably less than 20% by weight of the detergent composition.

Conventional detergent enzymes

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The detergent compositions can in addition to cholesterol esterase further comprise one or more enzymes which provide cleaning performance and/or fabric care benefits.

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Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, gluco-amylases, amylases, xylanases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, ß-glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof.

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A preferred combination is a detergent composition having cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

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The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, which discloses fungal cellulase produced from Humicola insolens. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

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Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800.

Other suitable cellulases are cellulases originated from Humicola insolens having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from Humicola insolens, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from Trichoderma longibrachiatum described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17243.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

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Preferred enhancers are substitued phenthiazine and phenoxasine 10-Phenothiazinepropionicacid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substitued syringates (C3-C5 substitued alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said cellulases and/or peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

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Amylases (α and/or ß) can be included for removal of carbohydrate-based stains. WO94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO94/18314, Genencor, published August 18, 1994 and WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in cleaning compositions include both α - and β -amylases. α -Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylase are stability-enhanced amylases including Purafact Ox Am^R described in WO 94/18314, published August 18, 1994 and WO96/05295, Genencor, published Februaury 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95.

Examples of commercial α -amylases products are Termamyl®, Ban® ,Fungamyl® and Duramyl®, all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α -amylase activity assay. Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Also included by definition, are mutants of native enzymes. Mutants can be obtained e.g. by protein and/or genetic engineering, chemical and/or physical modifications of native enzymes. Common practice as well is the expression of the enzyme via host organisms in which the genetic material responsible for the production of the enzyme has been cloned.

Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc... containing one enzyme) or as mixtures of two or more enzymes (e.g. cogranulates).

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful Bacillus, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Color care benefits

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Technologies which provide a type of color care benefit can also be included. Examples of these technologies are metallo catalysts for color maintenance. Such metallo catalysts are described in copending European Patent Application No. 92870181.2.

Other bleaching agent

One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of

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this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Application 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551.

Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

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The hydrogen peroxide releasing agents can be used in combination with other bleach activators such astetraacetylethylenediamine (TAED) or pentaacetylglucose (PAG), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect. Also suitable activators are acylated citrate esters such as disclosed in Copending European Patent Application No. 91870207.7.

Metal-containing catalysts for use in bleach compositions, include cobalt-containing catalysts such as Pentaamine acetate cobalt(III) salts and manganese-containing catalysts such as those described in EPA 549 271; EPA 549 272; EPA 458 397; US 5,246,621; EPA 458 398; US 5,194,416 and US 5,114,611. Bleaching composition comprising a peroxy compound, a manganese-containing bleach catalyst and a chelating agent is described in the patent application No 94870206.3.

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Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated

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and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.

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Useful bleaching agents, including peroxyacids and bleaching systems comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention are described in our copending applications WO95/27772, WO95/27774 and WO95/27775.

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Builder system

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates, alkyl- or alkenyl-succinic acid and fatty acids, materials such as ethylenediamine tetraacetate, diethylene triamine pentamethyleneacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B, HS or MAP.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate (Na₂Si₂O₅).

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Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent

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No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

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Alicyclic and heterocyclic polycarboxylates include cyclopentanecis, cis, cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5tetrahydro-furan - cis, cis, cis-tetracarboxylates, 2,5-tetrahydro-furan - cis dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6hexane -hexacar-boxylates and and carboxymethyl derivatives of polyhydric
alcohols such as sorbitol, mannitol and xylitol. Aromatic poly-carboxylates
include mellitic acid, pyromellitic acid and the phthalic acid derivatives
disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Preferred builder systems for use in the present compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid.

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Preferred builder systems include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid. Preferred builder systems for use in liquid detergent compositions of the present invention are soaps and polycarboxylates.

Other builder materials that can form part of the builder system for use in granular compositions include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

Other suitable water-soluble organic salts are the homo- or copolymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 5% to 80% by weight of the composition preferably from 10% to 70% and most usually from 30% to 60% by weight.

Chelant

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The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

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Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetraproprionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at lease low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Suds suppressor

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Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alcanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil^R.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

Others

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Other components used in detergent compositions may be employed, such as soil-suspending agents, optical brighteners, abrasives, bactericides,

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tarnish inhibitors, coloring agents, and/or encapsulated or non-encapsulated perfumes.

Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB 1,464,616.

Other suitable water soluble encapsulating materials comprise dextrins derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrins are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating material consists of a modified maize starch and glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2' disulphonate, disodium 4, - 4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino-stilbene-2:2' - disulphonate, disodium 4,4' - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2' - disulphonate, monosodium 4',4'' -bis-(2,4-dianilino-s-triazin-6 ylamino)stilbene-2-sulphonate, disodium 4,4'' -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2' - disulphonate, di-sodium 4,4' -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2' disulphonate, di-so-dium 4,4'bis(2-anilino-4-(1-ylamino)-s-triazol-2-yl)-stilbene-2,2' disulphonate, di-so-dium 4,4'bis(2-anilino-4-(1-ylamino)-s-triazol-2-ylamino)-s-triazol-2-ylamino-s-triazol-2

methyl-2-hydroxyethylamino)-s-triazin-6- ylami-no)stilbene-2,2'disulphonate, sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3 - triazole-2''-sulphonate and 4,4'-bis(2-sulphostyryl)biphenyl. Highly preferred brighteners are the specific brighteners of copending European Patent application No. 95201943.8.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

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Is is well-known in the art that free chlorine in tap water rapidly deactivates the enzymes comprised in detergent compositions. Therefore, using chlorine scavenger such as perborate, ammonium sulfate, sodium sulphite or polyethyleneimine at a level above 0.1% by weight of total composition, in the formulas will provide improved through the wash stability of the detergent enzymes. Compositions comprising chlorine scavenger are described in the European patent application 92870018.6 filed January 31, 1992.

polycarboxylates such as those Alkoxylated prepared polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per The side-chains are of the formula every 7-8 acrylate units. -(CH₂CH₂O)_m(CH₂)_nCH₃ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

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Softening agents

Fabric softening agents can also be incorporated into laundry detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0 299 575 and 0 313 146.

Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

Dye transfer inhibition

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The detergent compositions of the present invention can also include compounds for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

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Polymeric dye transfer inhibiting agents

The detergent compositions according to the present invention also comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.05% to 1% by weight of polymeric dye transfer inhibiting agents. Said polymeric dye transfer inhibiting agents are normally incorporated into cleaning compositions in order to inhibit the transfer of dyes from colored fabrics onto fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

Especially suitable polymeric dye transfer inhibiting agents are polyamine Noxide polymers, copolymers of Novinylpyrrolidone and Novinylimidazole, polyvinylpyrrolidone polymers, polyvinyloxazolidones and polyvinylimidazoles or mixtures thereof.

Addition of such polymers also enhances the performance of the enzymes according the invention.

a) Polyamine N-oxide polymers

The polyamine N-oxide polymers suitable for use contain units having the following structure formula:

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wherein P is a polymerisable unit, whereto the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.

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R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen

of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures:

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R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

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The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

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Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

One class of said polyamine N-oxides comprises the group of polyamine Noxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyrridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

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Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

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Preferred classes of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or

alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group.

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Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups.

Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

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The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a PKa < 10, preferably PKa < 7, more preferred PKa < 6.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

The N-vinylimidazole N-vinylpyrrolidone polymers used in the present invention have an average molecular weight range from 5,000-1,000,000, preferably from 5,000-200,000.

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Highly preferred polymers for use in detergent compositions according to the present invention comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000.

The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113, "Modern Methods of Polymer Characterization".

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Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have an average molecular weight range from 5,000 to 50,000; more preferably from 8,000 to 30,000; most preferably from 10,000 to 20,000.

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The N-vinylimidazole N-vinylpyrrolidone copolymers characterized by having said average molecular weight range provide excellent dye transfer inhibiting properties while not adversely affecting the cleaning performance of detergent compositions formulated therewith.

The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4.

35 c) Polyvinylpyrrolidone

The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most 5,000 preferably from about to about 15,000. Suitable polyvinylpyrrolidones are commercially vailable from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation Sokalan 165 Sokalan include HP and HP polyvinylpyrrolidones known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

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d) Polyvinyloxazolidone:

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The detergent compositions of the present invention may also utilize polyvinyloxazolidone as a polymeric dye transfer inhibiting agent. Said polyvinyloxazolidones have an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

e) Polyvinylimidazole:

The detergent compositions of the present invention may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles have an average about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most

f) Cross-linked polymers:

preferably from about 5,000 to about 15,000.

Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups n the backbone or on branches; cross-linked polymers have been described in the Journal of Polymer Science, volume 22, pages 1035-1039.

In one embodiment, the cross-linked polymers are made in such a way that they form a three-dimensional rigid structure, which can entrap dyes in the pores formed by the three-dimensional structure. In another embodiment, the cross-linked polymers entrap the dyes by swelling.

Such cross-linked polymers are described in the co-pending patent application 94870213.9

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Method of washing

The compositions of the invention may be used in essentially any washing or cleaning methods, including soaking methods, pretreatment methods and methods with rinsing steps for which a separate rinse aid composition may be added.

The process described herein comprises contacting fabrics with a laundering solution in the usual manner and exemplified hereunder.

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The process of the invention is conveniently carried out in the course of the cleaning process. The method of cleaning is preferably carried out at 5°C to 95°C, especially between 10°C and 60°C. The pH of the treatment solution is preferably from 7 to 11.

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A preferred machine dishwashing method comprises treating soiled articles with an aqueous liquid having dissolved or dispensed therein an effective amount of the machine diswashing or rinsing composition. A conventional effective amount of the machine dishwashing composition means from 8-60 g of product dissolved or dispersed in a wash volume from 3-10 litres.

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According to a manual dishwashing method, soiled dishes are contacted with an effective amount of the diswashing composition, typically from 0.5-20g (per 25 dishes being treated). Preferred manual dishwashing methods include the application of a concentrated solution to the surfaces of the dishes or the soaking in large volume of dilute solution of the detergent composition.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

In the detergent compositions, the enzymes levels are expressed by pure enzyme by weight of the total composition and unless otherwise specified, the detergent ingredients are expressed by weight of the total compositions. The abbreviated component identifications therein have the following meanings:

LAS : Sodium linear C₁₂ alkyl benzene sulphonate

TAS : Sodium tallow alkyl sulphate

CXYAS : Sodium C_{1X} - C_{1Y} alkyl sulfate

25EY : A C₁₂₋C₁₅ predominantly linear primary alcohol

condensed with an average of Y moles of ethylene

oxide

CXYEZ : A C₁X - C₁Y predominantly linear primary alcohol

condensed with an average of Z moles of ethylene

oxide

XYEZS : C₁x - C₁y sodium alkyl sulfate condensed with an

average of Z moles of ethylene oxide per mole

QAS : $R_2.N^+(CH_3)_2(C_2H_4OH)$ with $R_2 = C_{12}-C_{14}$

Soap

: Sodium linear alkyl carboxylate derived from a 80/20

mixture of tallow and coconut oils.

Nonionic

: C₁₃-C₁₅ mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5 sold under the tradename Plurafac LF404 by BASF Gmbh.

CFAA

: C₁₂-C₁₄ alkyl N-methyl glucamide

TFAA

: C₁₆-C₁₈ alkyl N-methyl glucamide.

TPKFA

: C12-C14 topped whole cut fatty acids.

DEQA

: Di-(tallow-oxy-ethyl) dimethyl ammonium chloride.

SDASA

: 1:2 ratio of stearyldimethyl amine:triple-pressed

stearic acid.

Neodol 45-13

: C14-C15 linear primary alcohol ethoxylate, sold by

Shell Chemical CO.

Tallow

Dihydrogenated tallowamidoethyl hydroxyethylmonium

methosulfate / glycol distearate / cetyl alcohol.

Silicate

: Amorphous Sodium Silicate (SiO₂:Na₂O ratio = 2.0)

NaSKS-6

: Crystalline layered silicate of formula δ-Na₂Si₂O₅

Carbonate

Anhydrous sodium carbonate with a particle size

between 200 μm and 900 μm .

Bicarbonate

: Anhydrous sodium bicarbonate with a particle size

between 400 μm and 1200 μm .

STPP

: Anhydrous sodium tripolyphosphate

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MA/AA : Copolymer of 1:4 maleic/acrylic acid, average

molecular weight about 80,000

PA30 : Polyacrylic acid of average molecular weight of

approximately 8,000.

Terpolymer : Terpolymer of average molecular weight approx.

7,000, comprising acrylic:maleic:ethylacrylic acid

monomer units at a weight ratio of 60:20:20

480N : Random copolymer of 3:7 acrylic/methacrylic acid,

average molecular weight about 3,500.

Polyacrylate : Polyacrylate homopolymer with an average molecular

weight of 8,000 sold under the tradename PA30 by

BASF GmbH

Zeolite A : Hydrated Sodium Aluminosilicate of formula

Na₁₂(A10₂SiO₂)₁₂. 27H₂O having a primary particle

size in the range from 0.1 to 10 micrometers

Citrate : Tri-sodium citrate dihydrate of activity 86,4% with a

particle size distribution between 425 μm and 850 μ

m.

Citric : Anhydrous citric acid

PB1 : Anhydrous sodium perborate monohydrate bleach,

empirical formula NaBO2.H2O2

PB4 : Anhydrous sodium perborate tetrahydrate

Percarbonate : Anhydrous sodium percarbonate bleach of empirical.

formula 2Na₂CO₃.3H₂O₂

TAED : Tetraacetyl ethylene diamine.

NOBS

: Nonanoyloxybenzene sulfonate in the form of the

sodium salt.

Photoactivated

Bleach

Sulfonated zinc phtlocyanine encapsulated in dextrin

soluble polymer.

PAAC

: Pentaamine acetate cobalt(III) salt.

Paraffin

: Paraffin oil sold under the tradename Winog 70 by

Wintershall.

BzP

Benzoyl Peroxide.

Cholesterol

esterase

Sigma bovine pancrease Cholesterol esterase (Sigma

3766) or Bohringar Mannheim Pseudomonas

fluorescens cholesterol esterase.

Protease

Proteolytic enzyme sold under the tradename

Savinase, Alcalase, Durazym by Novo Nordisk A/S,

Maxacal, Maxapem sold by Gist-Brocades and

proteases described in patents WO91/06637 and/or

WO95/10591 and/or EP 251 446.

Amylase

: Amylolytic enzyme sold under the tradename Purafact

Ox Am^R described in WO 94/18314, WO96/05295

sold by Genencor; Termamyl®, Fungamyl® and Duramyl®, all available from Novo Nordisk A/S and

those described in WO95/26397.

Lipase

: Lipolytic enzyme sold under the tradename Lipolase,

Lipolase Ultra by Novo Nordisk A/S

Cellulase

: Cellulytic enzyme sold under the tradename Carezyme,

Celluzyme and/or Endolase by Novo Nordisk A/S.

CMC

: Sodium carboxymethyl cellulose.

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HEDP: 1,1-hydroxyethane diphosphonic acid.

DETPMP : Diethylene triamine penta (methylene phosphonic

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acid), marketed by Monsanto under the Trade name

PCT/US96/20876

Dequest 2060.

PVNO : Poly(4-vinylpyridine)-N-Oxide.

PVPVI : Poly (4-vinylpyridine)-N-oxide/copolymer of vinyl-

imidazole and vinyl-pyrrolidone.

Brightener 1 : Disodium 4,4'-bis(2-sulphostyryl)biphenyl.

Brightener 2 : Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-

2-yl) stilbene-2:2'-disulfonate.

Silicone antifoam : Polydimethylsiloxane foam controller with siloxane-

oxyalkylene copolymer as dispersing agent with a ratio

of said foam controller to said dispersing agent of

10:1 to 100:1.

Granular Suds :

Suppressor

: 12% Silicone/silica, 18% stearyl alcohol, 70% starch

in granular form

SRP 1 : Sulfobenzoyl end capped esters with oxyethylene oxy

and terephtaloyl backbone.

SRP 2 : Diethoxylated poly (1,2 propylene terephtalate) short

block polymer.

SCS : Sodium cumene sulphonate

Sulphate : Anhydrous sodium sulphate.

HMWPEO : High molecular weight polyethylene oxide

PEG

: Polyethylene glycol.

BTA

: Benzotriazole

Bismuth nitrate

Bismuth nitrate salt

NaDCC

: Sodium dichloroisocyanurate

Encapsulated perfume particles

: Insoluble fragrance delivery technology utilising zeolite 13x, perfume and a dextrose/glycerin agglomerating

binder.

KOH

: 100% Active solution of Potassium Hydroxide

pН

: Measured as a 1% solution in distilled water at 20°C.

Example 1

The following laundry detergent compositions were prepared in accord with the invention:

	1	1)	lil	IV	V	VI
LAS	8.0	8.0	8.0	8.0	8.0	8.0
C25E3	3.4	3.4	3.4	3.4	3.4	3.4
QAS	•	0.8	0.8	-	0.8	0.8
Zeolite A	18.1	18.1	18.1	18.1	18.1	18.1
Carbonate	13.0	13.0	13.0	27.0	27.0	27.0
Silicate	1.4	1.4	1.4	3.0	3.0	3.0
Sulfate	26.1	26.1	26.1	26.1	26.1	26.1
PB4	9.0	9.0	9.0	9.0	9.0	9.0
TAED	1.5	1.5.	1.5	1.5	1.5	1.5
DETPMP	0.25	0.25	0.25	0.25	0.25	0.25
HEDP	0.3	0.3	0.3	0.3	0.3	0.3
Cholesterol	0.005	0.005	0.005	0.005	0.005	0.005
esterase						
Protease	0.0026	0.0026	0.0026	0.0026	0.0026	0.0026

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Amylase	-	0.0009	0.0009	0.0009	0.0009	0.0009
MA/AA	0.3	0.3	0.3	0.3	0.3	0.3
CMC	0.2	0.2	0.2	0.2	0.2	0.2
Photoactivated	15	15	15	15	15	15
bleach (ppm)						
Brightener 1	0.09	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5	0.5	0.5
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	850

Example 2

The following granular laundry detergent compositions of bulk density 750 g/litre were prepared in accord with the invention:

	I	li	181
LAS	5.25	5.61	4.76
TAS	1.25	1.86	1.57
C45AS	-	. 2.24	3.89
C25AE3S	-	0.76	1.18
C45E7	3.25	-	5.0
C25E3	-	5.5	-
QAS	0.8	2.0	2.0
STPP	19.7	-	-
Zeolite A	-	19.5	19.5
NaSKS-6/citric acid	-	10.6	10.6
(79:21)			
Carbonate	6.1	21.4	21.4
Bicarbonate	-	2.0	2.0
Silicate	6.8	-	-
Sodium sulfate	39.8	-	14.3
PB4	5.0	12.7	-
TAED	0.5	3.1	-
DETPMP	0.25	0.2	0.2
HEDP	-	0.3	0.3
Cholesterol esterase	0.005	0.005	0.005
Protease	0.0026	0.0085	0.045
Lipase	0.003	0.003	0.003

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	61		
Cellulase	0.0006	0.0006	0.0006
Amylase	0.0009	0.0009	0.0009
MA/AA	0.8	1.6	1.6
CMC	0.2	0.4	0.4
Photoactivated bleach (ppm)	15 ppm	27 ppm	. 27 ppm
Brightener 1	0.08	0.19	0.19
Brightener 2	-	0.04	0.04
Encapsulated perfume particles	0.3	0.3	0.3
Silicone antifoam Minors/misc to 100%	0.5	2.4	2.4

Example 3

The following detergent formulations, according to the present invention were prepared, where I is a phosphorus-containing detergent composition, II is a zeolite-containing detergent composition and III is a compact detergent composition:

	1	11	111
Blown Powder			
STPP	24.0	-	24.0
Zeolite A	-	24.0	-
C45AS	9.0	6.0	13.0
MA/AA	2.0	4.0	2.0
LAS	6.0	8.0	11.0
TAS	2.0	-	-
Silicate	7.0	3.0	3.0
CMC	1.0	1.0	0.5
Brightener 2	0.2	0.2	0.2
Soap	1.0	1.0	1.0
DETPMP	0.4	0.4	0.2
Spray On		•	
C45E7	2.5	2.5	2.0
C25E3	2.5	2.5	2.0
Silicone antifoam	0.3	0.3	0.3
Perfume	0.3	0.3	0.3
Dry additives			
Carbonate	6.0	13.0	15.0
PB4	18.0	18.0	10.0
PB1	4.0	4.0	0
TAED	3.0	3.0	1.0
Photoactivated bleach	0.02	0.02	0.02

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Cholesterol esterase	0.01	0.01	0.01
Protease	0.01	0.01	0.01
Lipase	0.009	0.009	0.009
Amylase	0.002	0.003	0.001
Dry mixed sodium sulfate	3.0	3.0	5.0
Balance (Moisture &	100.0	100.0	100.0
Miscellaneous)			
Density (g/litre)	630	670	670

Example 4

The following nil bleach-containing detergent formulations of particular use in the washing of colored clothing, according to the present invention were prepared:

Blown Powder	
Zeolite A 15.0 15.0	-
Sodium sulfate 0.0 5.0	-
LAS 3.0 3.0	~
DETPMP 0.4 0.5	-
CMC 0.4 0.4	-
MA/AA 4.0 4.0	-
Agglomerates	
C45AS	11.0
LAS 6.0 5.0	-
TAS 3.0 2.0	-
Silicate 4.0 4.0	-
Zeolite A 10.0 15.0	13.0
CMC	0.5
MA/AA	2.0
Carbonate 9.0 7.0	7.0
Spray On	
Perfume 0.3 0.3	0.5
C45E7 4.0 4.0	4.0
C25E3 2.0 2.0	2.0
Dry additives	
MA/AA	3.0
NaSKS-6	12.0
Citrate 10.0 -	8.0
Bicarbonate 7.0 3.0	5.0
Carbonate 8.0 5.0	7.0
PVPVI/PVNO 0.5 0.5	0.5
Cholesterol esterase 0.01 0.01	0.01

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	63		
Protease	0.026	0.016	0.047
Lipase	0.009	0.009	0.009
Amylase	0.005	0.005	0.005
Cellulase	0.006	0.006	0.006
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	9.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	700	700	700
Example 5		· · · ·	•

The following detergent formulations, according to the present invention were prepared:

	i	II	111	IV
LAS	20.0	14.0	24.0	22.0
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C25E5/C45E7		2.0	-	0.5
C45E3S	_	2.5	-	-
STPP	30.0	18.0	30.0	22.0
Silicate	9.0	5.0	10.0	8.0
Carbonate	13.0	7.5	-	5.0
Bicarbonate	-	7.5	-	-
DETPMP	0.7	1.0	-	-
SRP 1	0.3	0.2	-	0.1
MA/AA	2.0	1.5	2.0	1.0
CMC	0.8	0.4	0.4	0.2
Cholesterol esterase	0.01	0.01	0.01	0.01
Protease	0.008	0.01	0.026	0.026
Amylase	0.007	0.004	-	0.002
Lipase	0.004	0.002	0.004	0.002
Cellulase	0.0015	0.0005	-	-
Photoactivated	70ppm	45ppm	-	10ppm
bleach (ppm)				11
Brightener 1	0.2	0.2	0.08	0.2
PB1	6.0	2.0	-	-

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NOBS	2.0	1.0	-	-
Balance (Moisture	100	100	100	100
and Miscellaneous)				

Example 6

The following detergent formulations, according to the present invention were prepared:

	.	11	111	IV
Blown Powder				
Zeolite A	30.0	22.0	6.0	6.7
Na SkS-6	-	-	-	3.3
Polycarboxylate	-	-	-	7.1
Sodium sulfate	19.0	5.0	7.0	-
MA/AA	3.0	3.0	6.0	-
LAS	14.0	12.0	22.0	21.5
C45AS	8.0	7.0	7.0	5.5
Cationic	-	-	-	1.0
Silicate	-	1.0	5.0	11.4
Soap	-	-	2.0	-
Brightener 1	0.2	0.2	0.2	-
Carbonate	8.0	16.0	20.0	10.0
DETPMP	-	0.4	0.4	-
Spray On				
C45E7	1.0	1.0	1.0	3.2
Dry additives				
PVPVI/PVNO	0.5	0.5	0.5	-
Cholesterol esterase	0.01	0.01	0.01	0.01
Protease	0.052	0.01	0.01	0.01
Lipase	0.009	0.009	0.009	0.009
Amylase	0.001	0.001	0.001	0.001
Cellulase	0.0002	0.0002	0.0002	0.0002
NOBS	-	6.1	4.5	3.2
PB1	1.0	5.0	6.0	3.9
Sodium sulfate	-	6.0	- .	to balance

Balance (Moisture and 100 100 100 Miscellaneous)

Example 7

The following high density and bleach-containing detergent formulations, according to the present invention were prepared:

	1	11	HI
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sodium sulfate	0.0	5.0	15.0 0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DETPMP	0.4	0.4	0.4
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates		•	2.0
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
Dry additives			
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
TAED	6.0	2.0	5.0
PB1	14.0	7.0	10.0
Polyethylene oxide of MW	-	-	0.2
5,000,000		•	
Bentonite clay	-	-	10.0
Cholesterol esterase	0.01	0.01	0.01
Protease	0.01	0.01	0.01
Lipase	0.009	0.009	0.009
Amylase	0.005	0.005	0.005
Cellulase Silicopo antiform	0.002	0.002	0.002
Silicone antifoam Dry additives	5.0	5.0	5.0

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		66			
	Sodium sulfate	0.0	3.0	0.0	
Balance (Moist	ure and	100.0	100.0	100.0	
Miscellaneous)					
Density (g/litre)	850	850	850	

Example 8

The following high density detergent formulations, according to the present invention were prepared:

	1	li .
Agglomerate		
C45AS	11.0	14.0
Zeolite A	15.0	6.0
Carbonate	4.0	8.0
MA/AA	4.0	2.0
CMC	0.5	0.5
DETPMP	0.4	0.4
Spray On		
C25E5	5.0	5.0
Perfume	0.5	0.5
Dry Adds		
HEDP	0.5	0.3
SKS 6	13.0	10.0
Citrate	3.0	1.0
TAED	5.0	7.0
Percarbonate	20.0	20.0
SRP 1	0.3	0.3
Cholesterol esterase	0.01	0.01
Protease	0.014	0.014
Lipase	0.009	0.009
Cellulase	0.001	0.001
Amylase	0.005	0.005
Silicone antifoam	5.0	5.0
Brightener 1	0.2	0.2
Brightener 2	0.2	-

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Balance (Moisture and	100	100
Miscellaneous)		
Density (g/litre)	850	850

Example 9

The following granular detergent formulations, according to the present invention were prepared:

	I	11	111	IV.	
LAS	21.0	25.0	18.0	18.0	-
Coco C12-14 AS	-	-	-	-	21.9
AE3S	-	-	1.5	1.5	2.3
Decyl dimethyl	-	0.4	0.7	0.7	0.8
hydroxyethyl NH4+CI					
Nonionic	1.2	-	0.9	0.5	_
Coco C12-14 Fatty Alcohol	-	-	-	_	1.0
STPP	44.0	25.0	22.5	22.5	22.5
Zeolite A	7.0	10.0	-	-	8.0
MA/AA	-	-	0.9	0.9	-
SRP1	0.3	0.15	0.2	0.1	0.2
CMC	0.3	2.0	0.75	0.4	1.0
Carbonate	17.5	29.3	5.0	13.0	15.0
Silicate	2.0	_	7.6	7.9	-
Cholesterol esterase	0.01	0.01	0.01	0.01	0.01
Protease	0.007	0.007	0.007	0.007	0.007
Amylase	-	0.004	0.004	0.004	0.004
Lipase	0.003	0.003	0.003	-	_
Cellulase	-	0.001	0.001	0.001	0.001
NOBS	-	-	-	1.2	1.0
PB1	-	-	-	2.4	1.2
Diethylene triamine penta acetic acid	÷	-	-	0.7	1.0
Diethylene triamine penta methyl phosphonic acid	-	-	0.6	-	-
Mg Sulfate	•	_	0.8		_
Photoactivated bleach	45	50	15	45	42
	ppm	ppm	ppm	ppm	
Brightener 1	0.05	-	0.04	0.04	ppm 0.04
Brightener 2	0.1	0.3	0.05	0.13	0.13
Water and Minors	2	up to 10		· 0.10	0.10
······································		ap to 10	U /U		

Example 10

The following liquid detergent formulations, according to the present invention were prepared:

•	1	11	Ш	IV	٧	VI	VII	VIII
LAS	10.0	13.0	9.0	-	25.0	-	-	-
C25AS	4.0	1.0	2.0	10.0	-	13.0	18.0	15.0
C25E3S	1.0	-	-	3.0	-	2.0	2.0	4.0
C25E7	6.0	8.0	13.0	2.5	-	-	4.0	4.0
TFAA	-	-	-	4.5	<u>-</u> ·	6.0	8.0	8.0
QAS	-	-	-	-	3.0	1.0	-	-
TPKFA	2.0	-	13.0	2.0	*	15.0	7.0	7.0
Rapeseed fatty	-	-	-	5.0	-	-	4.0	4.0
acids								
Citric	2.0	3.0	1.0	1.5	1.0	1.0	1.0	1.0
Dodecenyl/	12.0	10.0	-	-	15.0	-	-	-
tetradecenyl								
succinic acid								
Oleic acid	4.0	2.0	1.0	-	1.0	-	-	-
Ethanol	4.0	4.0	7.0	2.0	7.0	2.0	3.0	2.0
1,2 Propanediol	4.0	4.0	2.0	7.0	6.0	8.0	10.0	13
Mono Ethanol	-	~	-	5.0	•	-	9.0	9.0
Amine								
Tri Ethanol	-	-	8	-	-	-	-	•
Amine								
NaOH (pH)	8.0	8.0	7.6	7.7	8.0	7.5	8.0	8.2
Ethoxylated	0.5	-	0.5	0.2	-	-	0.4	0.3
tetraethylene								
pentamine								
DETPMP	1.0	1.0	0.5	1.0	2.0	1.2	1.0	-
SRP 2	0.3	-	0.3	0.1	-		0.2	0.1
PVNO	-	-	-	-	-	-	-	0.10
Cholesterol	.005	.005	.005	.005	.005	.005	.005	.005
esterase								
Protease	.005	.005	.004	.003	0.08	.005	.003	.006
Lipase	-	.002	•	.000	-	-	.003	.003
				_				

Amylase	.002	.002	.005	.004	.002	.008	.005	.005
Cellulase	-	-	-	.000	-	-	.000	.000
				1			4	4
Boric acid	0.1	0.2	-	2.0	1.0	1.5	2.5	2.5
Na formate	-	-	1.0	-	-	-	-	_
Ca chloride	-	0.01	-	0.01	-	-	_	-
		5						
Bentonite clay		-	-	-	4.0	4.0	-	-
Suspending clay	-	-	-	-	0.6	0.3	_	_
SD3								
Balance	100	100	100	100	100	100	100	100
Moisture and								
Miscellaneous								

Example 11

Granular fabric cleaning compositions which provide "softening through the wash" capability were prepared in accord with the present invention:

	. 1	11
45AS	-	10.0
LAS	7.6	-
68AS	1.3	-
45E7	4.0	-
25E3	-	5.0
Coco-alkyl-dimethyl hydroxy-	1.4	1.0
ethyl ammonium chloride		
Citrate	5.0	3.0
Na-SKS-6	-	11.0
Zeolite A	15.0	15.0
MA/AA	4.0	4.0
DETPMP	0.4	0.4
PB1	15.0	_
Percarbonate	-	15.0
TAED	5.0	5.0
Smectite clay	10.0	10.0

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HMWPEO	-	0.1
Cholesterol esterase	0.01	0.01
Protease	0.02	0.01
Lipase	0.02	0.01
Amylase	0.03	0.005
Cellulase	0.001	-
Silicate	3.0	5.0
Carbonate	10.0	10.0
Granular suds suppressor	1.0	4.0
CMC	0.2	0.1
Water/minors	Up to 1	00%

Example 12

4 1) 7 8

The following rinse added fabric softener composition was prepared in accord with the present invention: 5

20.0
0.001
0.001
0.001
0.03
0.01
25ppm
0.20
0.90
%

Example 13

The following fabric softener composition was prepared in accord with 10 the present invention:

	1	H	111
DEQA	2.6	19.0	-
SDASA	-	-	70.0
Stearic acid of $IV = 0$	0.3	~	_
Neodol 45-13	-	-	13.0

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	71		
Hydrochloride acid	0.02	0.02	-
Ethanol	-	-	1.0
PEG	-	0.6	-
Cholesterol esterase	0.001	0.001	0.001
Perfume	1.0	1.0	0.75
Digeranyl Succinate	-	-	0.38
Silicone antifoam	0.01	0.01	-
Electrolyte	-	600ppm	-
Dye	100ppm	50ppm	0.01
Water and minors	100%	100%	

Example 14

Syndet bar fabric cleaning compositions were prepared in accord with the present invention:

	1	11	111	IV
C26 AS	20.00	20.00	20.00	20.00
CFAA	5.0	5.0	5.0	5.0
LAS (C11-13)	10.0	10.0	10.0	10.0
Sodium carbonate	25.0	25.0	25.0	25.0
Sodium pyrophosphate	7.0	7.0	7.0	7.0
STPP	7.0	7.0	7.0	7.0
Zeolite A	5.0	5.0	5.0	5.0
CMC	0.2	0.2	0.2	0.2
Polyacrylate (MW 1400)	0.2	0.2	0.2	0.2
Coconut monethanolamide	5.0	5.0	5.0	5.0
Cholesterol esterase	0.02	0.02	0.02	0.02
Amylase	0.01	0.02	0.01	0.01
Protease	0.3	-	0.5	0.05
Brightener, perfume	0.2	0.2	0.2	0.2
CaSO4	1.0	1.0	1.0	1.0
MgSO4	1.0	1.0	1.0	1.0
Water	4.0	4.0	4.0	4.0

Filler*: balance to 100%

*Can be selected from convenient materials such as CaCO3, talc, clay (Kaolinite, Smectite), silicates, and the like.

Example 15

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The following compact high density (0.96Kg/l) dishwashing detergent compositions I to VI were prepared in accord with the present invention:

	i	11	III	IV	V	VI
STPP	-	-	49.0	38.0	-	-
Citrate	33.0	17.5	-	-	54.0	25.4
Carbonate	-	17.5	-	20.0	14.0	25.4
Silicate	33.0	14.8	20.4	14.8	14.8	-
Metasilicate	-	2.5	2.5	• -	-	-
PB1	1.9	9.7	7.8	14.3	7.8	-
PB4	8.6	-	-	-	-	-
Percarbonate	-	-	-	-	-	6.7
Nonionic	1.5	2.0	1.5	1.5	1.5	2.6
TAED	4.8	2.4	2.4	-	2.4	4.0
HEDP	8.0	1.0	0.5	-	-	-
DETPMP	0.6	0.6	-	-	-	-
PAAC	-	-	-	0.2	-	-
BzP	-	-	-	4.4	~	-
Paraffin	0.5	0.5	0.5	0.5	0.5	0.2
Cholesterol esterase	0.01	0.01	0.01	0.01	0.01	0.01
Protease	0.075	0.05	0.10	0.10	0.08	0.01
Lipase	-	0.001	-	0.005	•	-
Amylase	0.01	0.005	0.015	0.015	0.01	0.0025
BTA	0.3	0.3	0.3	0.3	0.3	-
Bismuth Nitrate	-	0.3	-	-	-	-
PA30	4.0	-	-	-	-	-
Terpolymer	-	-	-	4.0	-	-
480N	-	6.0	2.8	-	-	-
Sulphate	7.1	20.8	8.4	-	0.5	1.0
pH (1% solution)	10.8	11.0	10.9	10.8	10.9	9.6

10 <u>Example 16</u>

The following granular dishwashing detergent compositions examples I to IV of bulk density 1.02Kg/L were prepared in accord with the present invention:

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J

	i	11	111	IV	V	VI
STPP	30.0	30.0	30.0	27.9	34.5	26.7
Carbonate	30.5	30.5	30.5	23.0	30.5	2.80
Silicate	7.4	7.4	7.4	12.0	8.0	20.3
PB1	4.4	4.4	4.4		4.4	-
NaDCC	-	-	-	2.0	-	1.5
Nonionic	0.75	0.75	0.75	1.9	1.2	0.5
TAED	1.0	1.0	-	-	1.0	-
PAAC	-	-	0.004	-	-	-
BzP	~	1.4	-	-	_	
Paraffin	0.25	0.25	0.25	-	-	-
Cholesterol esterase	0.01	0.01	0.01	0.01	0.01	0.01
Protease	0.05	0.05	0.05	-	0.1	-
Lipase	0.005	-	0.001	-	-	_
Amylase	0.003	0.001	0.01	0.02	0.01	0.015
BTA	0.15	-	0.15	-	-	-
Sulphate	23.9	23.9	23.9	31.4	17.4	-
pH (1% solution)	10.8	10.8	10.8	10.7	10.7	12.3

Example 17

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The following detergent composition tablets of 25g weight were prepared in accord with the present invention by compression of a granular dishwashing detergent composition at a pressure of 13KN/cm² using a standard 12 head rotary press:

•	1 .	Ħ	Ш
STPP	-	48.8	47.5
Citrate	26.4	-	-
Carbonate	-	5.0	-
Silicate	26.4	14.8	25.0
Cholesterol esterase	0.01	0.01	0.01

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	74		
Protease	0.03	0.075	0.01
Lipase	0.005	-	-
Amylase	0.01	0.005	0.001
PB1	1.6	7.8	-
PB4	6.9	-	11.4
Nonionic	1.2	2.0	1.1
TAED	4.3	2.4	0.8
HEDP	0.7	-	-
DETPMP	0.65	-	-
Paraffin	0.4	0.5	-
BTA	0.2	0.3	-
PA30	3.2	-	-
Sulphate	25.0	14.7	3.2
pH (1% solution)	10.6	10.6	11.0

Example 18

The following liquid dishwashing detergent compositions were prepared in accord with the present invention I to II, of density 1.40Kg/L:

	I	II
STPP	33.3	20.0
Carbonate	2.7	2.0
Silicate	-	4.4
NaDCC	1.1	1.15
Nonionic	2.5	1.0
Paraffin	2.2	-
Cholesterol esterase	0.01	0.01
Protease	0.03	0.02
Amylase	0.005	0.0025
480N	0.50	4.00
КОН	-	6.00
Sulphate	1.6	-
pH (1% solution)	9.1	10.0

CLAIMS

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- 1. A detergent composition comprising a cholesterol esterase at a level of from 0.0001% to 5%, preferably 0.001% to 2% pure enzyme by weight of total composition.
- 2. A detergent composition according to claim 1 further comprising a nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactant.

3. A detergent composition according to claims 1 to 2 further comprising a lipolytic enzyme.

- 4. A detergent composition according to claims 1 to 3 further comprising a proteolytic enzyme.
 - 5. A detergent composition according to any of the preceding claims further comprising a hydrophobic bleach activator.
- 20 6. A detergent composition according to any of the preceding claims further comprising a dispersant.
 - 7. A detergent composition according to any of the preceding claims further comprising a soil release polymer.
 - 8. A detergent composition according to any of the preceding claims further comprising other detergent enzymes, preferably an amylase and/or cellulase.
- A detergent composition according to claim 1 which is in the form of an additive.
- 10. A fabric softening composition comprising a cholesterol esterase at a level of from 0.0001% to 5%, preferably 0.001% to 2% pure enzyme by weight of total composition and a cationic surfactant comprising two long chain lengths.

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11. Use of a detergent composition according to any of the preceding claims for fabric detergent and/or fabric stain removal and/or fabric whiteness maintenance and/or fabric softening and/or fabric color appearance and/or fabric dye transfer inhibition.

12. Use of a detergent composition according to claims 1 to 9 for hand and machine dishwashing.

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INTERNATIONAL SEARCH REPORT

Intern: al Application No PCT/US 96/20876

A. CLAS	SIFICATION OF SUBJECT MATTER		
IPC 6	C11D3/386		
According	to International Patent Classification (IPC) or to both national classification	and the state of t	
	S SEARCHED	assilication and IPC	
Minimum	documentation searched (classification system followed by classifi	ication symbols)	
IPC 6	C11D		
Document	ation searched other than minimum documentation to the extent th	at such documents are included in the fields	searched
,			
	•		
Electronic	data base consulted during the international search (name of data	hase and, where practical, search terms used	
	MENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the	e relevant passages	Relevant to claim No.
Χ	US A 011 160 A ADIEUL EDANGES I		
^	US 4 011 169 A (DIEHL FRANCIS L 8 March 1977	. El AL.)	1-3,8
	see column 3, line 45 - line 65		
	see column 15, line 66 - line 68	3	
	see claims; examples		
Х	DATABASE WPI		1
	Section Ch, Week 9534		, L
	Derwent Publications Ltd., Londo	on, GB;	
	Class B04, AN 95-260033 XP002038199		
	& JP 07 163 339 A (TOYOBO KK)	
	27 June 1995	, ,	
	see abstract		
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	egories of cited documents:	T later document published after the inte	mational filing date
"A" docume	ent defining the general state of the art which is not ered to be of particular relevance	cited to understand the principle or the	h the annication but
	document but published on or after the international	"X" document of particular relevance; the	
"L" docume	nt which may throw doubts on priority claim(s) or	cannot be considered novel or cannot involve an inventive step when the doc	he considered to
citation	s cited to establish the publication date of another or other special reason (as specified)	Y document of particular relevance: the	daimed invention
O docume	ent referring to an oral disclosure, use, exhibition or neans	document is combined with one or mo	re other such docus
"P" docume	nt published prior to the international filing date but an the priority date claimed	ments, such combination being obvious in the art. '&' document member of the same patent in	
Date of the a	actual completion of the international search	Date of mailing of the international sea	
		or are with the 252	2 on report
20	August 1997	0 8. 09 97	,
Name and m	ailing address of the ISA	Authorized officer	
	European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk		
	Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Serbetsoglou, A	
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INTERNATIONAL SEARCH REPORT

Intern. 1 Application No
PCT/US 96/20876

		PCT/US 96/20876
C.(Continua	tion) DOCUMENTS CONSIDERED TO BE RELEVANT	
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